

## **5000 Series Alloys With Improved Corrosion Properties and Methods for Their Manufacture and Use**

### CROSS REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims priority from U.S. Provisional Application Serial No. 60/399,134 filed July 30, 2002, the content of which is incorporated herein by reference in its entirety.

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

[0002] The present invention relates generally to 5000 series aluminum alloys and particularly to such alloys having high strength, good corrosion resistance and are lightweight.

#### 2. Description of Related Art

[0003] Al-Mg sheet products, as delivered, especially those in H1x tempers are generally well resistant to most forms of corrosion. ASTM standard B928 allows one to determine resistance to corrosion, especially intergranular and exfoliation corrosion, of sheet products. However, it is well known that products in these alloys can develop sensitivity to intergranular corrosion, exfoliation corrosion or stress corrosion as a result of inappropriate processing or long term exposure to moderate temperatures, the range of interest generally being regarded as from 80 – 200°C. Thus, several months at 80°C, or several weeks at 100°C, or even several days at 130°C can suffice to “sensitize” the material to the aforementioned forms of corrosion. This so-called “sensitization effect” limits the application of these alloys to situations where it is possible to guarantee they will be exposed for only short-times to temperatures in the aforementioned

ranges. In order to evaluate propensity to such sensitization, laboratory corrosion tests are frequently performed after so-called “sensitization treatments”, which are intended to simulate what would actually occur upon longer term exposure at lower temperatures (that is, simulating in-service thermal exposure). A microstructural phenomenon underlying this sensitivity to intergranular corrosion in conventional alloys as is known in the art, is the precipitation of a continuous layer of binary Al-Mg phase (so-called  $\beta$ -phase), the composition of which is usually given as  $Mg_2Al_3$ , at grain boundaries.

[0004] One of the more widely-used 5000 series alloys is designated Al-5083, that contains, in addition to aluminum, approximately 4.5 wt% magnesium and 0.7% wt% manganese. The following references are mentioned here as background and are expressly incorporated herein by reference in their entireties:

1. Sprowls, D.O. and Brown, R.H., in Stress Corrosion Mechanisms for Aluminum Alloys, Fundamental Aspects of Stress Corrosion Cracking, NACE, p.466-504 (1969).
2. Speidel, M.O. and Hyatt, M.V., in ed. M.G. Fontana and R.W. Staehle, Plenum Press: New York, (1972).
3. Aluminum Standards and Data, The Aluminum Association, Inc.: Washington, DC (1993).
4. Massalski, T.B., Binary Phase Diagrams, American Society for Metals: Metals Park, OH (1986).
5. Moore, M.R., in Marine Inspection Advisory, ed. Seattle, WA, (2002).
6. Samson, S., Acta Cryst. 19, 401-413 (1965).
7. Auld, J.H. and Williams, B.E., Acta Cryst. 21, 830-831 (1966).
8. Wheeler, M.J., Blankenburgs, G. and Staddon, R.W., Nature 207, 746-747 (1965).

9. Vetrano, J.S., Danielson, M.J., Baer, D.R. and Jones, R.H., in *Microchemistry and Microstructural Aspects Leading to Stress Corrosion Cracking in AA5083, Automotive Alloys 2000*, TMS, (1999).
10. Searles, J.L., in *AA5083*. Dept. of Materials Science and Engineering, ed. The Ohio State University: Columbus, OH, p.109 (2000).
11. Carroll, M.C., Gouma, PL, Mills, M.J., Daehn, G.S. and Dunbar, B.R., *Scripta Mat.* 42, 335-340 (1999).
12. Auld, W., *Acta Crystallogr.* 21, 830 (1966).
13. Carroll, M.C., Gouma, PL, Daehn, G.S. and Mills, M.J., in *Copper additions to 5083*, ICSMA 12, (2000).
14. Ratchev, P., Verlinden, B. and P VanHoutte, *Scripta Metall.* 30, 599-604 (1994).
15. *Br. Corr. J.* (6), (1971).
16. Carroll, M.C., in *Improvements to Str. Corr. Res. of AA5083*. Materials Science and Engineering, ed. The Ohio State University: Columbus, p.250 (2001).
17. Dif, R., Ehrstrom, J.C. and Raynaud, G.M., in *The effect of zinc additions on the corrosion properties of aluminum alloy*, ICAA-6, p.1489-1494 (1998).

[0005] In order to increase the range of versatility of 5083, a number of modifications have been examined that could potentially improve the strength and corrosion resistance characteristics while maintaining a chemical composition that is very close to the proven 5083 alloy. WO 97/38146 entitled "Aluminum Magnesium Alloy Plate or Extrusion" describes high strength Al-Mg alloys and the content of this document is incorporated herein by reference in its entirety.

[0006] As mentioned above, many of the prior art 5XXX series alloys are not sufficiently corrosion resistant, *inter alia* due to the formation of binary beta phase particles at grain boundaries that precipitate upon simulated medium temperature sensitization treatments. On the other hand, when Zn is added without copper in a 5XXX alloy, a ternary Al-Mg-Zn phase (so-called "ternary tau phase") forms that results in a product that is typically insufficient in terms of stress corrosion cracking properties. This ternary phase, once formed, seems in fact, more electrochemically active than beta. Thus, according to the prior art, it was believed that it was not possible to obtain a non-heat treatable high strength 5XXX alloy as such an alloy would be corrosion prone, especially if exposed to extreme sensitization conditions that would inevitably occur in use, for example, in automotive or marine applications.

#### SUMMARY OF THE INVENTION

[0007] It would be highly desirable to obtain a Al-Mg based alloy that maintains generally recognized benefits of 5XXX alloys (such as weldability, formability, overall good resistance to corrosion, low cost processing), but in addition displays a significantly reduced propensity to become corrosion-sensitive even after having been subjected to a severe sensitization treatment. In particular, it would be highly desirable to obtain a material resistant to stress corrosion cracking, demonstrable by the fact that there is little, if any difference between (i) elongation in air and (ii) elongation in the environment the material is subjected to during a slow strain rate test (SSRT).

[0008] In accordance with these and other objects, the present invention is directed to an Al-Mg alloy (5XXX alloy) wherein upon being subjected to a sensitization treatment, a quaternary Al-Mg-Zn-Cu phase (so-called "quaternary tau phase") is formed at grain boundaries, as opposed to the generally observed binary Al-Mg phase ( $\beta$ -phase) which is precipitated at grain boundaries in conventional Al-Mg alloys, or the ternary Al-Mg-Zn  $\tau$ -phase observed in Al-Mg alloys with Zn additions.

[0009] Preferably the alloy includes from 0.05-0.2% Cu, from 3.5 – 6.5% Mg, more preferably from 3.8 or 3.9 – 6.5% Mg, from 0.4 to 1.0 % Mn, and from 0.05-0.2% Cu. However, the present invention is directed to any Al-Mg alloy that forms such a quaternary tau phase at grain boundaries as well as applications comprising such alloys including but not limited to marine products, railcar products, dump bodies, chemical tank cars, cryogenic applications and/or auto body panels, to name a few. The present invention is further directed to methods for making Al-Mg alloys having the above-mentioned quaternary (preferably tau) phase and methods for their implementation and use.

[00010] In advantageous embodiments, the magnesium content is controlled between 3.5 and 5.0%, preferably between about 3.8 or 3.9 and 5.0 %.

[00011] In particularly preferred embodiments, the alloys comprise or consist essentially of

Cu 0.05-0.2%;

Zn 0.3-0.6%;

Mg 4.0-5.0%;

Mn 0.4-1.0%;

Cr 0-0.3%

Incidental impurities; and

Al balance.

[00012] In some embodiments, it is possible to optionally include Ag 0.03-.23% if desired for any reason.

[00013] The formation of a quaternary phase during moderate temperature exposure has been observed to coincide with improved resistance to corrosion after sensitization treatments.

[00014] Additional objects, features and advantages of the invention will be set forth in the description which follows, and in part, will be obvious from the description, or may be learned by practice of the invention. The objects, features and advantages of the invention may be realized and obtained by means of the instrumentalities and combination particularly pointed out in the appended claims.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[00015] The accompanying drawings, which are incorporated in and constitute a part of the specification, illustrate a presently preferred embodiment of the invention, and, together with the general description given above and the detailed description of the preferred embodiment given below, serve to explain the principles of the invention.

[00016] Figure 1 is a composition map of 5083+Cu that demonstrates some discrete Al-Mg-Cu particles at grain boundary, but Mg-rich binary  $\beta$ -phase are present.

[00017] Figure 2 is an EDS spectra of grain boundary phase in Zn+Cu-containing sample demonstrates observable levels of copper and zinc.

[00018] Figure 3 depicts a digital image of the grain boundary phases and associated composition maps of selected grain boundary area; elemental mapping developed from developing EDS spectra over a scanned area (EMiSPEC maps) show relative levels of selected elements; brighter areas indicate higher concentration; copper is present in addition to the expected levels of magnesium and zinc.

[00019] Figure 4 shows a diffraction pattern (a) of  $\alpha$ -aluminum matrix and Al-Mg-Zn-Cu precipitate; simulation (b), based on an  $\text{Mg}_{32}(\text{Al,Zn})_{49}$  precipitate in aluminum, agrees well with

the observed pattern.

- [00020] Figure 5 shows needle-shaped Cu-containing precipitates prevalent in the high-copper sample (inset (b) shows a close-up view); present in small amounts in the medium-copper sample and absent in the low-copper sample.
- [00021] Figure 6 is a high-resolution Transmission Electron Microscopy (TEM) image of one aspect of an additional phase precipitate; associated Fourier transform (inset) of CCD (charge-coupled device) image correlates very well with S-phase published work.
- [00022] Figure 7 shows micrographs of 5083 + Zn + medium silver; micrograph (a) and Scanning Transmission Electron Microscopy (STEM) image (b) demonstrate the grain boundary phase, while the presence of silver, along with Mg and Zn, is clear from the composition maps (c).
- [00023] Figure 8 shows micrographs of 5083 + Zn + high copper and silver; micrograph (a) and STEM image (b) demonstrate the grain boundary phase; composition maps (c) show that a 5-component phase with both copper and silver present.
- [00024] Figure 9 shows the high density of precipitates in the grain interior that is present even in the alloys containing relatively low additions of Ag; the presence of a distinct precipitate-free zone is also demonstrated.
- [00025] Figure 10 demonstrates Slow Strain Rate Testing (SSRT) results of inventive alloys vs. standard 5083.
- [00026] Figure 11 depicts a Constant Extension Rate Testing (CERT) result for an inventive alloy in dry air vs. NaCl environment; the inventive alloy has less initial ductility than standard 5083,

but more of this ductility is retained with respect to SM.

[00027] Figure 12 shows characteristic shapes of failure regions of tensile samples; Stress Corrosion Cracking (SCC) failure demonstrates a stepped series of stress drops rather than the gentle downward curve of engineering stress.

[00028] Figure 13 shows that by increasing the annealing treatment from 10-15 minutes to 75 minutes in some embodiments of the present invention decreases the ductility of 5083 both in air and in aqueous NaCl (a), but increases elongation to failure in air (in inventive alloys (b-d)).

[00029] Figure 14 shows Stress/strain curves for sensitized vs. unsensitized alloys pulled in air at 10-3/second; inset shows detail of yield point and associated increase in yield strength for inventive alloys.

[00030] Figure 15 shows Fine-probe Energy Dispersive Spectrum (EDS) that reveals the presence of Zn, Cu and Ag in the grain boundary region even at a reduced Zn level.

[00031] Figure 16 is a composition map of a reduced-Zn embodiment; the grain boundary phase is in the Al<sub>6</sub>Mn/grain boundary interface.

[00032] Figure 17 is a deflection and shows CERT (aqueous NaCl) results of inventive alloys showing Zn level.

[00033] Figure 18 shows an advantageous window with respect to SCC failure for low-level additions in Zn-modified 5083 alloys.

[00034] Figure 19a and b show grain structures of a Scanning Electron Microscopy (SEM) image



according to an embodiment of the present invention wherein 19a is a general view of the grain structure and 19b is a decoration of the grain boundaries of Al-Mg-Zn-Cu precipitates .

[00035] Figure 20 shows Al-Mg-Zn-Cu precipitates at numeral 2 (corresponding to Fig. 22a) and numeral 3 shows Al-Mg matrix (corresponding to figure 22b)

[00036] Figure 21 shows Al-Mg-Cu-Zn precipitates at numeral 4 as shown in Fig. 22c spectra.

[00037] Figures 22a, b and c are spectra corresponding to the micrographs of Figures 20 and 21.

#### DETAILED DESCRIPTION OF A PREFERRED EMBODIMENT

[00038] It has unexpectedly been found that combined and controlled Zn and Cu additions to Al-Mg alloys (such as typically 5XXX series aluminum alloys) improve corrosion resistance of high strength magnesium alloys, particularly after being subject to severe thermal sensitization (actual or simulated). Commercial applications include marine products, railcar products, dump body, chemical tank cars (rail/trailer), cryogenic applications and auto body panels (inner/outer). A detailed discussion of additional methods, properties and methods according to the present invention are described in "Improvements to the Strength and Corrosion Resistance of Al-Mg-Mn Alloy of Near-AA5083 Chemistry," PhD Thesis of M.C. Carroll, Oct. 30, 2001, the content of which is incorporated herein by reference in its entirety.

[00039] It has unexpectedly been found that quaternary tau phase generated in the presence of Cu has an electrochemical potential that renders the product resistant to intergranular, exfoliation and stress corrosion cracking in various corrosive environments.

[00040] Moreover, it has unexpectedly been found that products in which a quaternary tau phase

is generated at the grain boundaries in AlMg based alloys after long term exposure to medium temperatures, have improved resistance to intergranular, exfoliation and stress corrosion cracking in various corrosive environments, and are particularly resistant to sensitization during such thermal exposure.

[00041] The evolution of high-speed waterborne transports, particularly the latest generation of passenger and automobile ferries, has generated a larger demand for quality aluminum alloys that can meet performance and design requirements in terms of strength, weldability, formability, and corrosion resistance. Al-5083 is one alloy that can meet these design guidelines, but potential problems exist in Al-Mg alloys with Mg concentrations greater than 3.5 wt% .see Sprowls, D.O. and Brown, R.H., in Stress Corrosion Mechanisms for Aluminum Alloys, Fundamental Aspects of Stress Corrosion Cracking, NACE, p.466-504 (1969), and Speidel, M.O. and Hyatt, M.V, in ed. M.G. Fontana and R.W Staehle, Plenum Press: New York, (1972).]. 5083 is one alloy that falls into this category, with ASTM guidelines for composition levels falling between 4.0 and 4.9 wt%. This level is well above the supersaturation level in a binary Al-Mg system (with a solvus of approx. 3.0 wt% at 200 degrees C.)

[00042] Magnesium provides appreciable increases in alloy strength from a solid solution strengthening mechanism well into the supersaturation region. The drawback, however, is that this supersaturated solid solution in the matrix will eventually decompose, with a binary Al-Mg  $\beta$  phase ( $\text{Al}_3\text{Mg}_2$ ) precipitating out, particularly at grain boundaries and at large Mn or impurity-based particle interfaces. The resulting precipitate structure and compositional gradients can lead to an aggressive electrochemical attack at the grain boundaries, resulting in a weakening of the grain boundary regions and premature failure when subjected to tensile stress. This phenomenon, known as “intergranular corrosion” as well as situations where the material is subjected to concurrent mechanical loading, stress corrosion cracking (SCC), is of particular concern if the right thermal conditions have generated a corrosion-susceptible microstructure or

if the environment provides a catalyst for electrochemical attack. In the case of the microstructure, the most susceptible alloy is one whereby some level of thermal energy has led to the extended formation of  $\beta$  phase at grain boundaries. It is known that the  $\beta$ -phase is strongly anodic to aluminum in a variety of electrolytes. The thermal conditions for  $\beta$ -phase evolution, known as a sensitization, need only be moderate temperatures over a period of time. As for the SCC-enhancing environment, clearly an application for these alloys such as use in fast ferry construction, which leaves the alloys exposed to seawater essentially over the life of their service, would fall into this category.

[00043] The need for further understanding of this potential mechanism for premature failure has been brought back to the forefront very recently by the rapid deterioration and fracture of a particular production run of Al-5083 plate used in a number of high-speed passenger vessels. The concern over these failures has led to a marine inspection advisory from the U.S. Coast Guard concerning the construction and inspection of vessels and the types of marine-grade alloys that are recommended [see Moore, M.R., in Marine Inspection Advisory, ed. Seattle, WA, (2002)].

[00044] Zinc additions to a standard Al-5083 appear to be effective in totally supplanting Al-Mg  $\beta$ -phase formation in favor of ternary  $\tau$ -phase under a variety of conditions. The occupation of different sites within the  $\tau$ -phase unit cell is such that different ratios of Al and Zn are possible for the same crystallographic structure. The  $\tau$ -phase is therefore the dominant, or even exclusive, phase that forms, even at very low levels of Zn content in the alloy. Previous success with zinc additions has been shown at levels at or above 0.7 wt% Zn, but effective grain boundary phase modification was evident with Zn levels as low as 0.3 wt%.

[00045] Zinc additions alone are not sufficient in combating SCC susceptibility in these high-Mg alloys. Under testing conditions that simulated the worst possible microstructural state (*i.e.*

intermetallic grain boundary phases had been allowed to form extensively), the Zn-containing alloys proved to be less resistant than standard Al-5083 under the same testing conditions. Corrosion potential curves on bulk grain boundary intermetallic phases (binary  $\beta$ - and ternary  $\tau$ -phase) confirmed that under similar anodic conditions, the corrosion current density of ternary  $\tau$ -phase would be much higher.

[00046] The  $\tau$ -phase can be modified in a way that the  $\beta$ -phase cannot, owing to the solubility of Cu at different levels in a Zn-containing  $\tau$ -phase. During CERT testing, standard 5083 alloys modified with Zn additions along with copper levels between approximately 0.08 and 0.12 wt% unexpectedly demonstrated considerable gains in ductility to failure under severe SCC-susceptible conditions.

[00047] Losses in the dry-air ductility of the inventive alloys indicate that some extra hardening is resulting from precipitate formation owing to the alloy additions. While the role of Ag in SCC resistance is unclear, there was a measurable increase in precipitation in grain interiors following Ag additions to the inventive alloys. This dry-air loss in ductility, however, indicates that the correctly modified alloys may, in fact, be more resistant to SCC failure than indicated by SCC ductility alone. The amount of retained ductility as a fraction of dry-air ductility is fractionally much higher than that of standard Al-5083 under the same conditions.

[00048] While the addition of Zn + Cu has very favorable results under the severe conditions outlined above, these modifications also aid in SCC resistance under less severe conditions or in other processed states, such as in different tempers or following weld cycles.

[00049] While the failures identified above were described as having included a high degree of exfoliation, failures due to SCC alone are potentially of much greater concern. In Al-Mg alloys, both types of material degradation are attributable to corrosive attack of grain boundary regions.

Exfoliation, however, is a surface condition that is readily observable, while failures due to SCC can be sudden and catastrophic with no indication of prior weakening. For this reason, the present inventors endeavored to examine possible changes to the grain boundary chemistry that made the alloy less susceptible to SCC failure, even under the most extreme conditions. These conditions include an extended degree of sensitization designed to produce the most potentially susceptible microstructure, and the least favorable SCC conditions-tensile stress to failure under constant extension rate while being exposed to an aqueous NaCl environment. The present invention is directed to modifications to the chemistry of Al-5083 through minor additions of Zn, Cu, and optionally Ag, added in amounts that are low enough that the favorable bulk properties of Al-5083 are altered to a very minor degree. Additionally, the inventive alloys described herein were processed in a manner that is designed to be representative of commercially-produced and processed Al-5083 sheet in an H116 temper so as to prove their suitability for end uses contemplated herein.

#### Zn Additions

[00050] The potentially beneficial effect of Zn additions may be attributable to the ease to which a ternary Zn-containing  $\tau$ -phase,  $Mg_{32}(Al,Zn)_{49}$ , will form in what otherwise would be Al-Mg  $\beta$ -phase forming conditions. The  $\beta$ -phase is largely confined to the grain boundaries and to particle interfaces, in no small part due to its high degree of disregistry within the lattice as well as the energetically-favorable conditions that such locations provide with respect to interfacial energy. The complex  $\beta$ -phase unit cell, which has been reported to contain 1168 atoms [see Samson, S., *Acta Cryst.* 19, 401-413 (1965)] is a face-centered cubic structure with a lattice parameter of approximately 2.82 nm. The Zn-based  $\tau$ -phase is also body-centered with a lattice parameter of only about 1.4 nm [see Auld, J.H. and Williams, B.E., *Acta Cryst.* 21, 830-831 (1966).] Also inherent in the Zn-based  $\tau$ -phase is an apparent robustness with regard to Zn:Al ratios. The ease to which  $\tau$ -phase will form was also evaluated with respect to minimizing Zn levels in the alloy.

Cu and Ag Additions

[00051] Like Zn, a crystallographic  $\tau$ -phase can form in these ternary systems that has a similar structure and lattice parameter as that of Zn-based  $\tau$ -phase; 1.44 nm for Ag-based  $\tau$ -phase [see Wheeler, M.J., Blankenburgs, G. and Staddon, R.W, Nature 207, 746-747 (1965).] and 1.435 nm for Cu-based  $\tau$ -phase. Evident from the published stoichiometry for each phase is the apparent ratio that is less robust with respect to aluminum content in the phase. The unit cell stoichiometry for Ag-based  $\tau$ -phase is  $\text{Al}_6\text{AgMg}_4$  while for Cu-based tau phase it is  $\text{Al}_5\text{CuMg}_4$ .

[00052] In accordance with the present invention, elemental additions were found that formed suitable advantageous preferable composition windows based on precipitation events and grain boundary phase morphology. Based on the compositions that demonstrated clear changes in what is potentially a SCC-controlling microstructure, tests were performed in order to create an appropriate correlation between SCC-resistant performance and the observed microstructures.

[00053] In accordance with the present invention, there is provided an Al-Mg based alloy (*i.e.* a 5xxx alloy) that maintains the generally recognized benefits of this family of alloys (weldability, formability, overall good resistance to corrosion, and lower cost processing at the sheet or plate supplier), but in addition displays a significantly reduced propensity to become corrosion-sensitive, even after being subjected to severe sensitization. The present invention provides, *inter alia*, an unexpected benefit obtained by combined additions of Cu and Zn to Al-Mg alloys. Microstructural analysis indicates that the beneficial effect coincides with the formation during the sensitization of a quaternary Al-Mg-Zn-Cu phase (“quaternary  $\tau$ -phase”) at grain boundaries as opposed to the generally observed binary  $\beta$ -phase (Al-Mg) which is precipitated at grain boundaries in conventional alloys or the ternary  $\tau$ -phase (Al-Mg-Zn) observed in such alloys with Zn additions. In accordance with one embodiment, an improvement in resistance to sensitization coincided with a specific Cu range for the alloys. However, it is believed that all alloys of an

appropriate stoichiometry develop this phase during medium temperature thermal exposure, and hence will show this benefit. Thus, alloys with as low concentrations as 3.5% or even 3% Mg, which have a thermodynamic driving force to precipitate Mg-containing phases at grain boundaries because of the supersaturated nature of the solid solution at the aforementioned temperatures, will benefit from additions of Zn and Mg. In particular preference in some embodiments are those materials have a Zn content of 3.9% or less.

[00054] Other alloy additions can be expected to favor the formation of quaternary  $\tau$ -phase. For example, Ag (among others) demonstrates this effect. Thus, the addition of Ag or any other quaternary tau-phase contributor to such alloys may also be beneficial in some embodiments.

[00055] Figures 1-9 demonstrate that the addition of Cu alone to 5083 type alloys does not eliminate the formation of  $\beta$ - phase at grain boundaries (Figure 1). However, combined additions of Cu+Zn favor the formation of a quaternary phase at the grain boundaries (Figures 2-4). When excess copper is added (Figures 5-6) the presence of an S-phase is detected. Figures 8 and 9 show the microstructural effect of adding silver, both on grain boundary precipitation (Fig. 8) and intragranular precipitation.

[00056] Figure 13 shows increased ductility in Figures 13b-d with improved SCC resistance. However, as this test is performed in air for b-d, the increased ductility just demonstrates increase ductility, which is nevertheless of interest in and of itself. Figure 18 demonstrates that the alloys that form quaternary phases have elongations in NaCl solution virtually identical to those in air (*i.e.* approximately 15%, see Figure 13 for example). This lack of reduction in elongation in NaCl vs. testing in air is one important indicator of improved SCC resistance.

## EXAMPLES

[00057] Examples described herein are illustrative and representative of advantageous

embodiments and are not intended to limit the invention in any way.

#### Experimental Conditions

[00058] It was an object of the present invention to produce a worthwhile modification to a popular alloy that could essentially be modified while employing the already-established industrial production practice. To this end, the alloys observed were all cast with a commercial-grade 5083 as a base material, with measured additions of zinc, copper, and/or silver. 5083 was re-melted in an induction furnace and previously-cast master alloys containing the "modification" elements were added following a complete melt of the base alloy. The newly modified alloys were then re-cast in a graphite mold in 2 x 2 x 6 in. ingots. The substantial shrinkage cavity was scalped from the ingots prior to a homogenization treatment and a hot work reduction at 450 +/- 50°C. A cold work reduction of 20% was then applied followed by a flash anneal, the goal of which was to produce a temper representative of a standard H116. While careful control of pre-cast measurements was strictly followed in order to obtain modified alloys at the composition levels desired, all alloys were re-evaluated for composition levels via elemental spectroscopy. The measured compositions for each of the alloys described is based on results obtained by dissolving small amounts of cast samples taken from various locations of a representative section of each ingot.

[00059] Previous work by Vetrano [see Vetrano, J.S., Danielson, M.J., Baer, D.R. and Jones, R.H., in *Microchemistry and Microstructural Aspects Leading to Stress Corrosion Cracking in AA5083*, Automotive Alloys 2000, TMS, (1999)] and by Searles [see Searles, J.L., in *AA5083*. Dept. of Materials Science and Engineering, ed. The Ohio State University: Columbus, OH, p.109 (2000)], demonstrated the high degree of dependence of SCC performance on the control of the sensitization treatment. Based on the results of this work, it was shown that there exists a degree of sensitization whereby further heat treatment will not degrade SCC performance, and in



fact some degree of resistance will be regained through extending the heat treatments to longer times. The standard sensitization treatment given to all samples for this study was 165°C for 175 hours. This treatment was applied in order to produce what would potentially be the most SCC-susceptible microstructure -long enough for grain boundary phases to fully form but not so long that further coarsening would lead to a recovery of SCC-resistant ductile properties.

[00060] For the microstructural observations, two transmission electron microscopes (TEMs) were employed. One, a Philips CM200 LaB<sub>6</sub>, was used for microstructural observations and diffraction data as well as for fine-probe energy-dispersive spectroscopy (EDS). The second microscope, a Philips CM300 FEG, was employed for high-resolution TEM (HRTEM) observations as well as for high magnification compositional mapping via Emispec's ES Vision data acquisition software when operated in scanning TEM (STEM) mode. All thin foils were prepared by dimpling to 25 µm and ion milling on a Gatan dual stage ion mill at 6kV, 1 mA, in order to retain as much of the physical structure of the grain boundary phases as possible. Previous work had demonstrated that electrochemical thinning via jet polishing severely degraded the corrosion-susceptible grain boundary microstructure [see Carroll, M.C., Gouma, P.L., Mills, M.J., Daehn, G.S. and Dunbar, B.R., Scripta Mat. 42, 335-340 (1999)].

[00061] For evaluating SCC performance, constant extension rate testing (CERT) was performed on the alloys after being machined into cylindrical tensile samples. Each sample was pulled to failure in tension at a rate of 10<sup>-6</sup>/sec-slow enough to allow the SCC mechanism to operate as the main mode of failure but not so slow that repassivation of corrosion-susceptible surfaces was mitigating factor. For true evaluation of SCC performance for marine-grade applications, samples were immersed for the duration of the test in a 0.5M aqueous NaCl solution in order to simulate full exposure to a seawater-based marine environment.

#### Compositional Mapping

[00062] One of the more important characteristics of the inventive alloys goes back to the aforementioned propensity to forming  $\tau$ -phase rather than  $\beta$  at grain boundaries when Zn is present. Because the stoichiometry does not require a strict ratio of Zn to Al, the presence of various levels Zn in 5083 has been shown to invariably lead to the exclusive formation of  $\tau$ -phase at grain boundaries. Such behavior was not observed for singular copper or silver additions, whereby ternary phases did form, but this was in addition to the widespread formation of grain boundary  $\beta$ -phase. Figure 1 demonstrates this phenomenon in a sample to which a high level of copper (0.53 wt%), but no zinc, was added. The discrete particles at the grain boundary contain copper, but magnesium enrichment ( $\beta$ -phase or  $\beta$ -phase precursor) still readily exists in an extended or continuous morphology along the boundary. In Zn-containing variants, maps demonstrate that these extended grain boundary phases are always comprised of Zn in addition to Al and Mg. Based on the earlier success of Zn additions to Al-Mg alloys under lightly sensitized conditions, [see Carroll, M.C., Gouma, P.L., Mills, M.J., Daehn, G.S. and Dunbar, B.R., Scripta Mat. 42, 335-340 (1999).] all samples modified and subsequently studied following the observation of the discrete particles in Cu-or Ag-exclusive samples contained some level of zinc. This was in order to ensure that phases that formed at grain boundaries were invariably some form of  $\tau$ -phase, and not combinations of discrete particles and Al-Mg  $\beta$ -phase.

	Mg wt %	Mn wt %	Zn wt %	Cu wt %
Low Cu	4.1	.49	.58	.073
Med Cu	4.3	.50	.62	0.13
High Cu	4.4	.51	.58	0.24

Table 1: Compositions of re-cast 5083-based alloys with about 0.6 wt% Zn and varying levels of Cu.

Cu + Zn Additions

[00063] Since it was determined that Zn additions were important for grain boundary modification of these 5083-based alloys, a series of alloys were cast that contained a moderate level of Zn (approximately 0.6 wt%) along with a varying level of Cu. The compositions for these castings can be seen in Table 1. Fine-probe Energy Dispersive Spectrum (EDS) analysis reveals the presence of both copper and zinc in the fully-formed grain boundary phases (Figure 2).

[00064] Compositional maps (Figure 3) indicate the presence of copper in these grain boundary regions even at the lowest copper level; it therefore follows that copper, which can form  $\tau$ -phase along with Al and Mg, is also quite soluble in the more robust Zn-containing  $\tau$ -phase. In addition to the composition information, diffraction patterns, d-spacing measurements [see Auld, W., *Acta Crystallogr.* 21, 830 (1966)] , and simulations via Desktop Microscopist confirm that these phases that form are indeed a quaternary Al-Mg-Zn-Cu,  $\tau$ -phase (Figure 4).

[00065] Of immediate concern in the copper modified alloys was the presence of large numbers of needle-shaped precipitates in the sample containing the highest level of copper (0.24 wt%)[see Carroll, M.C., Gouma, P.I., Daehn, G.S. and Mills, M.J., in *Copper additions to 5083*, ICSMA 12, (2000)]. These precipitates, shown in Figure 5, were predominantly in the grain interiors, in regions outside the vicinity of grain boundaries. High Resolution Transmission Electron Microscopy (HRTEM) analysis (Figure 6) and associated Fourier simulations compared with published work by other authors [see Ratchev, P., Verlinden, B. and P VanHoutte, *Scripta Metall.* 30, 599-604 (1994)] revealed these phases to be the  $\text{Al}_2\text{MgCu}$  S-phase. A small number of these additional phases were also observed sporadically in the "medium" copper level sample, containing 0.13 wt% Cu. A great deal of study was given to the corrosion mechanisms associated with S-phase in Al-Cu 2000 series alloys due to the deleterious effects readily associated with it. The unwanted presence of S-phase precipitates therefore provided a preferable general "upper boundary" for Cu additions in a Zn-modified 5083 alloy-at concentration levels near or above the level of the "medium" copper sample, or approximately 0.13 wt%.

	Mg wt %	Mn wt %	Zn wt %	Ag wt %
Low Ag	4.3	.50	.60	0.10
Med Ag	4.3	.50	.55	0.23

Table 2 : Compositions for a silver-modified 5083 + Zn alloy; Ag levels are based on Cu levels.

Low Mg Examples

[00066] In another embodiment of the present invention, the quaternary Al-Mg-Zn-Cu phase was also found in 3 mm thick sheet in O temper (sample reference I) made in an alloy with the composition Mg 3.8 wt%, Zn 0.40 wt%, Mn 0.40 wt%, Cu 0.15 wt% after a thermal treatment of 1000 hours at 110 °C. These phases occurred at the grain boundaries. Their size was about 0.1 to 1  $\mu\text{m}$ . The mass loss according to ASTM G 67 was 26.7  $\text{mg}/\text{cm}^2$ . Preferably the mass loss is less than about 40  $\text{mg}/\text{cm}^2$ , or in some embodiments less than about 27 $\text{mg}/\text{cm}^2$ . In other embodiments, it may be advantageous for the mass loss to even be less than about 15  $\text{mg}/\text{cm}^2$ . The quaternary phase does not occur in conventional 5XXX Al-Mg alloys such as 5019, 5182, 5754 or 5454.

[00067] Table 3 shows results of corrosion test (mass loss according to ASTM G 67) of 3 mm thick sheets (thickness 3 mm) in O-temper after 1000 hours of sensitization at 110 °C in various alloys.

Table 3 :

Sample	Mg [wt %]	Cu [wt %]	Zn [wt %]	Mn [wt %]	Cr [wt %]	Ti [wt %]	Mass loss [mg/cm <sup>2</sup> ]
A	3.99	0.15	0.4	0.1	0.1	0.15	42
B	3.85	0.07	0.4	0.4	0	0.15	40.9
C	3.99	0.15	0.2	0.4	0.1	0	42.6
D	3.96	0.07	0.4	0.1	0.1	0.15	37.5
E	4.04	0.07	0.2	0.4	0	0.15	43.9
F	4.09	0.07	0.2	0.1	0.1	0	32.8
G	3.99	0.15	0.2	0.1	0	0.15	42.5
H	4.00	0.15	0.4	0.1	0	0	27.2
I	3.82	0.15	0.4	0.4	0	0	26.7
J	3.91	0.07	0.4	0.4	0.1	0	30.0
K	3.99	0.15	0.2	0.4	0.1	0.15	49.4
L	4.05	0.07	0.2	0.1	0	0	30.4
R1	4.09	0	0	0.25	0	0	38.1
R2	4.07	0	0	0.55	0.1	0	40.6

S (AA5019)	5.18						58.7
T (AA5182)	4.61						46.6
U (AA5182)	4.64						47.3
W (AA5754)	2.81						11.2

[00068] Samples S, T, U and W are in H24 temper (S) or O/F temper ; T was a sheet 6 mm thick, whereas U, V and W were 4 mm sheet.

[00069] It can be seen from these results that products according to the present invention have an improved corrosion resistance compared to products with similar magnesium content. This is believed to be due to the quaternary phase which contains Al, Mg, Cu and Zn. See Figures 19-22 that detail the microstructure, and composition of the precipitates that formed according to sample I. This microstructural and compositional data in Figs 19-22 is believed to be comparable across the inventive alloy compositional ranges.

[00070] It was particularly surprising that for Mg=4.0% cases; all such samples showed higher weight losses, including case A (4%Mg, 0.15%Cu, 0.4% Zn, 0.1%Mn, 0.1%Cr) which might apart from a detrimental effect of Ti) have been expected to perform well. Below is a condensed table showing Mg=4%, and which demonstrates the trend of an improved performance of the Cu+Zn containing variants vs. R1 and R2 (no Cu or Zn). Particularly preferably, superior performance is shown at 0.15%Cu and 0.4%Zn (see H and I)

Sample	Mg [wt %]	Cu [wt %]	Zn [wt %]	Mn [wt %]	Cr [wt %]	Ti [wt %]	Mass loss [mg/cm <sup>2</sup> ]
C	3.99	0.15	0.2	0.4	0.1	0	42.6
F	4.09	0.07	0.2	0.1	0.1	0	32.8
H	4	0.15	0.4	0.1	0	0	27.2
I	3.82	0.15	0.4	0.4	0	0	26.7
J	3.91	0.07	0.4	0.4	0.1	0	30
L	4.05	0.07	0.2	0.1	0	0	30.4
R1	4.09	0	0	0.25	0	0	38.1
R2	4.07	0	0	0.55	0.1	0	40.6

Table 4

Ag + Cu + Zn Additions

[00071] Based on the information gained from observations on the Cu + Zn samples, a set of alloys was produced that contained Ag in levels that approximated the wt% of the Cu-containing alloys-the "low" and "medium" samples. Compositions for these alloys are given in Table 2. Like the Cu-based modified alloys,  $\tau$ -phase forms extensively that contains some level of silver, even at the lowest levels. A compositional map of an Ag + Zn-containing alloy is shown in Figure 7.

[00072] Both Cu and Ag are soluble in a Zn-containing  $\tau$ -phase in modified 5083 alloys and a set of castings that contained both Cu and Ag in addition to the Zn at the usual target level of 0.6 wt% was made. Compositions of these alloys are given in Table 3. Compositional maps reveal the solubility of the additional elements in the Zn-based  $\tau$ -phase. The resulting grain boundary phase, like that shown in Figure 8, is a five-constituent  $\tau$ -phase containing levels of Al, Mg, Zn,

Cu, and Ag, with a likely stoichiometric representation of  $Mg_{32}(Al,Zn,Cu,Ag)_{49}$ .

	Mg wt %	Mn wt %	Zn wt %	Cu wt %	Ag wt %
Low	4.3	.50	.60	0.05	0.10
High	4.3	.50	.55	0.10	0.20

Table 5 : Compositions for a silver- and copper-modified 5083 + Zn alloy.

[00073] Indeed a modification of the grain boundary phase has been demonstrated through these instant additions. It should be noted that in the Ag-modified alloys, a considerable amount of excess precipitation is evident in grain interiors, as shown for example, in Figure 9. A distinct precipitate-free zone approximately 250 nm wide is also evident. Cu and Ag, like Zn, combine with Al and Mg to form  $\tau$ -phase. From a practical standpoint, this should be considered when evaluating the merit of Ag additions that part of the "balance of properties", which includes cost, that makes Al-5083 an attractive alloy in many applications could possibly be compromised through additions of more expensive elements. Such a profound effect on precipitate distribution should generally be considered with regard to associated changes to other bulk properties.

[00074] In another series of trials, that are detailed in the Oct. 30, 2001 Carroll thesis mentioned *supra* several alloys the composition of which is given in Table 6 were recast from 5083 with minor element (Zn, Cu, Ag) addition. The ingots were hot worked (90 % reduction) and cold worked (20 % reduction), followed by a stabilization anneal yielding properties close to those obtained in H116 temper. Sensitization treatment was performed at 165°C for 175 hours. SSRT testing was performed in 3.5% NaCl on cylindrical specimens of diameter 0.15". Results are listed in Table 7.



Reference	Mg (wt%)	Mn (wt%)	Zn (wt%)	Cu (wt%)	Ag (wt%)
S1	3.9	0.52	0.20	0.08	0.05
S2	4.3	0.50	0.55	0.12	0.04
S3	3.9	0.55	0.20	0.13	
S4	4.4	0.53	0.30	0.06	0.03
S5	4.1	0.49	0.58	0.073	
S6	4.2	0.50	0.60		
5083 ref	4.2	0.5			

Table 6 : Compositions for testing of effectiveness of combined Zn+Cu and Zn+Cu+Ag additions

Reference	Description	SSRT strain to failure
S1	Low Zn + High Ag + High Cu	0.097
S2	Zn + Ag + Medium Cu	0.133
S3	Zn + High Cu	0.115
S4	Ag + Medium Cu	0.145
S5	Zn + Low Cu	0.041
S6	High Zn	0.042
5083 ref	Standard 5083	0.094

Table 7 : SSRT testing results for alloys listed in table 6

[00075] It can be seen that alloy S6 performed rather poorly. Surprisingly, a decrease in magnesium from 4.2 to 3.9%, a decrease in zinc from 0.60 to 0.20% and addition of 0.14% Cu lead to a significant improvement (alloy S3). The addition of 0.03% silver (alloy S4) lead to a very good performance in the SSRT test, compared to standard 5083 material according to the prior art. Alloys without Ag but with relatively low Mg (below about 4.2% for example), would

be expected to perform similarly to alloy S6.

Constant Extension Rate Testing (CERT)

[00076] The microstructural information is of interest since it can be appropriately correlated with various material properties of interest. Properties of most interest in with these particular inventive alloys is their ability to resist failure due to SCC. For the evaluation of SCC susceptibility, the employment of CERT in an aqueous NaCl environment provides not only an indication of the inherent resistance of the material to failure under SCC conditions, but is also effective in providing a comparison of other bulk properties to standard A1-5083. Such properties include for example, stiffness, yield strength, work hardening rate, and ductility.

[00077] Figure 10 shows a series of CERT results from various inventive alloys compared directly with 5083. It can be seen that for most sensitization conditions for standard 5083, several modified alloys perform better and several perform worse. Among those performing worse were the samples that contained either Zn alone or Zn and a very minor level of copper. Also notable from these plotted results are the shift in work hardening rates for the modified alloys-a clear product of additional solid solution strengtheners along with an increased density of excess precipitates.

[00078] In terms of direct SCC performance, the samples performing most poorly were samples where the dominant grain boundary phase was Zn-dominated. The copper modification has an apparent effect on the SCC-to-failure susceptibility of these alloys. There is a clear demonstration of the effect of Zn on these alloys in the absence of Cu. While earlier work may have pointed to a beneficial effect of Zn in these alloys under moderate levels of sensitization, for the instant alloys, however, the level of sensitization they can be subjected to is extreme. Fully

formed ternary  $\tau$ -phase does, in fact, have a considerably higher corrosion rate even than original  $\beta$ -phase. This behavior is confirmed by electrochemical potential curves generated for both phases. The indication is therefore that in that Zn alone only has a positive corrosion-resistant effect under moderate sensitization situations. Moderate sensitization is much less than what a product is subjected to in use in automotive and marine applications as well as others typical 5XXX applications. In fact, with respect to products that reach a heavily sensitized state, Zn can actually exacerbate SCC susceptibility problems. The positive copper effect is realized when sufficient copper is added to overcome the corrosion-prone behavior of fully-formed Zn-based  $\tau$ -phase. Note that an advantageous performance can be obtained by "medium" copper additions—further increases in Cu may instigate additional S-phase formation that may have an effect on performance in some situations. A preferable composition according to one embodiment are alloys wherein copper additions are high enough to overcome the deleterious effects of Zn additions alone following  $\tau$ -phase formation, but are also low enough to avoid additional S-phase formation.

[00079] Additional consideration must be given to a comparison of the alloys in the corrosive environment vs. those pulled to failure in air. Standard Al-5083, in the processed condition outlined above, demonstrates a drop in ductility to failure from about 23% in dry air to less than 10% in aqueous NaCl in a fully-sensitized condition. Since there can be some change in bulk characteristics from the alloy modifications, from Figure 11 it is clear that indeed a drop in "dry-air" ductility is apparent for the inventive alloy that performed well in the SCC-enhanced environment. As mentioned *supra*, the dry-air ductility of 5083 was near 23%, while the ductility of the inventive alloy under similar conditions was only about 14.5%. When immersed in aqueous NaCl, the ductility of fully-sensitized 5083 plummets to below 10% when failure occurs, while the inventive alloy retained an extremely high fraction of its dry-air ductility. Extension to failure, therefore, is not entirely descriptive of the inventive alloys' resistance to SCC susceptibility and subsequent failure.

[00080] A comparison of the retained ductility between dry conditions and aqueous NaCl reveals that inventive alloys are actually much more resistant to an SCC-based degradation in performance than simple ductility to failure in a corrosive environment alone would indicate. As long as the post-processed ductility values for inventive alloys are within acceptable design restrictions, a suitable evaluation of SCC performance is a comparison of the alloy's performance both in dry conditions and in representative corrosive conditions. For standard 5083 that has been fully sensitized, this test shows the drop in ductility to failure from dry air to aqueous NaCl of about 60%. For the inventive alloy in Figure 11, the drop is less than 10%. Some insight into the failure mechanism of the inventive alloys can also be gained by observing the shape of the CERT curve at failure. In an SCC mechanism, the propagation of a crack along corrosion-weakened grain boundaries would be expected to exhibit the step-wise drops in applied stress until total fracture occurs, as demonstrated in the more "corrosion-prone" alloys. These would include standard 5083 as well as the Zn-only modified alloys.

[00081] Those alloys demonstrating good resistance to failure under SCC conditions often demonstrate more of a gradual decrease in engineering stress followed by failure with none of the propagating crack characteristics of SCC-prone alloys (Figure 12). This behavior was seen in those alloys that maintained a large degree of their dry-air ductility as well as those assumed to be weakened through extensive S-phase formation-the high-copper samples.

#### Excess Precipitation Behavior

[00082] Regarding the changes in bulk properties, advantageous corrosion properties were evident while the basic characteristics of Al-5083 were largely maintained. Building on the observations concerning an apparent loss of ductility in dry air, there is a measurable degree of change in the inventive alloy behavior as a non-age-hardenable alloy. The trend in alloy response following the post-processing anneal reveals that some level of ductility in the alloy is recoverable through an extended anneal. The goal behind the "flash" anneal was to relieve some of the dislocation

strain energy following the cold work, an effect that might occur more naturally during reductions in an industrial setting. In each of the inventive alloys shown in Figure 13, the extended anneal treatment caused an increase in dry-air ductility, while standard 5083 (Figure 13(a)) demonstrates a clear decrease. The extra precipitate structure in the inventive alloys give them some degree of heat treatability, a characteristic shown by the increased work hardening rate following sensitization (Figure 14) of the inventive alloys that is not seen in 5083. A post cold work full anneal can therefore be expected to re-solutionize and homogenize the excess solute composition. Previous work has shown that extended heat treatments at elevated temperatures in standard 5083 serve only to nucleate and grow more of the manganese-based secondary precipitates, Al<sub>6</sub>Mn, as well as to coarsen existing particles [see Carroll, M.C., in Improvements to Str. Corr. Res. of AA5083. Materials Science and Engineering, ed. The Ohio State University: Columbus, p.250 (2001)] None are effectively driven back into solution.

#### Reduced Zn Samples

[00083] A propensity for large T-phase particles associated with high levels of Zn in Al-Mg alloys to leads to hot cracking problems during casting and processing of ingots. Welding of Zn-containing 5000 series alloys can lead to severely anodic, and therefore corrosion-prone, solute-depleted areas in the heat affected zones. [see Dif, R., Ehrstrom, J.C. and Raynaud, G.M., in The effect of zinc additions on the corrosion properties of aluminum alloy, ICAA-6, p.1489-1494 (1998)] Thus, inventive alloys containing a reduced amount of Zn were subjected to SCC resistance testing. Microstructural changes and subsequent SCC performance of Al-5083 modified with only 0.3 wt% Zn rather than the previously studied 0.6 wt% was made. One of the initial positive responses of Zn in these inventive alloys was the robustness to which they allowed  $\tau$ -phase to form, completely supplanting  $\beta$ -phase formation. Further-reduced levels of Zn may also provide exclusive -T-phase formation, and the inventive alloys can be further modified with Cu to form SCC-resistant alloys as desired. The composition for the reduced Zn samples are shown in Table 4. Again, samples were cast with a range of copper that proved to

envelope the positive effects regarding corrosion resistance along with the suppression of any significant population density of S-phase precipitates. Each of the samples was once again aggressively sensitized to allow the grain boundary phases to fully form and provide an SCC-susceptible condition. Microstructural investigations via fine probe EDS (Figure 15) as well as compositional mapping (Figure 16) indicate that the Zn influences the phase that forms at grain boundaries. CERT testing (Figure 17) reveals behavior that is similar to that in the alloys containing the higher concentration of Zn-some window exists whereby ductility to failure under SCC conditions is greatly improved over standard A1-5083 depending on the level of copper available to modify the Zn-based  $\tau$ -phase. Copper levels that are too high or too low allow other mechanisms to dominate the failure mode, and may be ineffective at improving the SCC response compared to standard 5083 alloy in some situations.

#### Copper Levels

[00084] For both 0.3 and 0.6% Zn, it was shown that one or more advantageous copper composition windows exists for maximizing the inventive alloy's resistance to SCC failure under the corrosive CERT conditions outlined above. Figure 18 demonstrates the apparent peak in ductility based on Cu content for a number of conditions, including varying Zn levels as well as hardened (unrecrystallized) material. Again, these conditions included a level of sensitization that was assumed throughout to be the worst case marine-service scenario, based on results from standard A1-5083 testing on alloys that were processed to obtain an H116-type temper. The copper levels considered as advantageous in some embodiments fall within a range that may be more easily obtained for alloys cast in 600 gram batches than those direct-chill cast in an industrial setting into 20,000 kg ingots.

[00085] Additional advantages, features and modifications will readily occur to those skilled in the art. Therefore, the invention in its broader aspects is not limited to the specific details, and

representative devices, shown and described herein. Accordingly, various modifications may be made without departing from the spirit or scope of the general inventive concept as defined by the appended claims and equivalents thereof, both foreseeable and unforeseeable.

[00086] As used herein and in the following claims, articles such as “the”, “a” and “an” can connote the singular or plural.